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SAN DIEGO STATE UNIV CA DEPT OF CHEMISTRY
W H RICHARDSON 31 MAR 85 ARO-17283.8-CH
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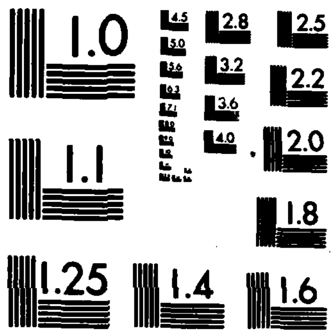

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Most of the research deals with the effect of electronic structural variation upon the efficiency of triplet state carbonyl production from dioxetanes. Other studies involving dioxetanes include the question of preferential n,π^* state (vs π,π^*) carbonyl formation and attempts to trap the proposed 1,4-dioxybiradical intermediate from thermolysis of dioxetanes. Some amino peroxides were also studied as potential sources of chemilumuniscence (CL). Finallly, a detailed kinetic study was made on the thermolysis of a five-membered ring peroxide in order to distinguish between concerted vs stepwise decomposition routes. This study was pertinent to the mechanism of dioxetane (a four-ring peroxide) thermolysis.

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Item 7. Publications.

1. W.H. Richardson and D.L. Estberg, "Substituent Effects upon the Efficiency of Excited State Acetophenones Produced on Thermolysis of 3,4-Diaryl-3,4-dimethyl-1,2-dioxetanes", J. Org. Chem., submitted for publication.

2. W.H. Richardson and S.A. Thomson, "Substituent Effects on Excited State Efficiencies: Thermolysis of 3,3-(o,)-Biphenylyl)-4-methyl-4-aryl-1,2-dioxetanes", J. Org. Chem. 1985, 50, xxxx, accepted for publication.

3. W.H. Richardson, in "The Chemistry of Functional Groups. Peroxide-Acidity, Hydrogen Bonding, and Complex Formation", S.Patai, Ed., Wiley, 1983.

4. W.H. Richardson and D.L. Stiggall-Estberg, "Electronic Effects on Triplet and Singlet Carbonyl Formation in the Thermolysis of 3-Aryl-3-methyl-1,2-dioxetane", J. Am. Chem. Soc., 104, 4173 (1982).

5. W.H. Richardson and S.A. Thomson, "A Search for Electron-Transfer Decomposition and the Production of Electronically Excited State Species in the Thermolysis of p-Dimethylaminophenyl Substituted Dialkyl Peroxides", J. Org. Chem., 47, 4515 (1982).

6. W.H. Richardson, "Haloaromatic Substituted Olefins by the McMurry Olefin Synthesis", Synthetic Communications, 11, 895 (1981).

7. W.H. Richardson, R. McGinness, and H.E. O'Neal, "Kinetics and Mechanism of the Thermolysis of a Five-membered Ring Peroxide, 3,3,5,5-Tetramethyl-1,2-dioxolane", J. Org. Chem., 46, 1887 (1981).

8. W.H. Richardson, "Energy Sufficient α-Amino Peroxides as Potental Sources of Excited-State Carbonyls", J. Org. Chem., 45, 303 (1980).

Item 8. Scientific personnel:

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Research Findings

Most of the research described here deals with the effect of electronic structural variation upon the efficiency of triplet state carbonyl production from dioxetanes. Other studies involving dioxetanes include the question of preferential n,π^* state (vs π,π^*) carbonyl formation and attempts to trap the proposed 1,4-dioxybiradical intermediate from thermolysis of dioxetanes. Some amino peroxides were also studied as potential sources of chemilumuniscence (CL). Finallly, a detailed kinetic study was made on the thermolysis of a five-membered ring peroxide in order to distinguish between concerted vs stepwise decomposition routes. This study was pertinent to the mechanism of dioxetane (a four-ring peroxide) thermolysis.

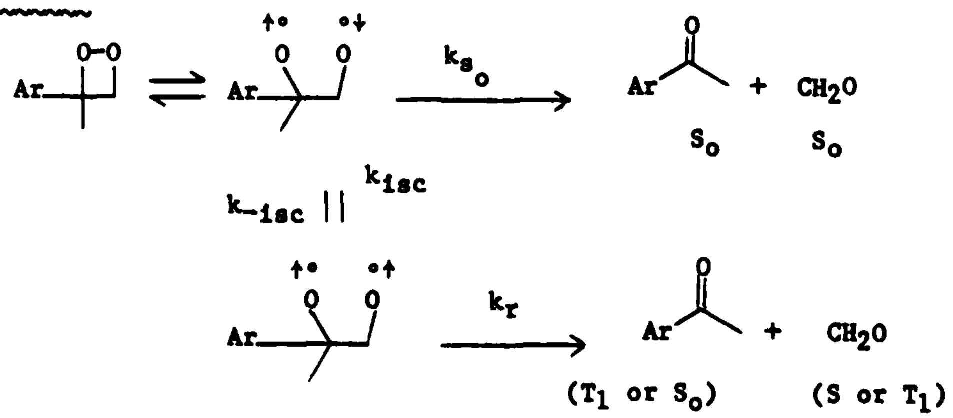
Dioxetane Structure vs Efficiency of Excited State Production. This study is limited to simply substituted dioxetanes, ie, those dioxetanes which have no easily oxidized substitutents such as amino or phenoxide. Previous work suggested a stepwise biradical pathway for the thermolysis of these simply substituted dioxetanes. It is now well-known that this type of dioxetane produces largely triplet rather than excited state singlet carbonyl product.

Our earlier work indicated that both steric and electronic effects contributed to variations in triplet carbonyl production from dioxetanes. These changes can be significant with triplet efficiencies (α_T) ranging from about 0.1% to possibly as high as 60%. Thus, there is considerable interest to determine how these steric and electronic effects mediate changes in α_T.

In this research, a study of electronic effects on α_T was emphasized, where steric effects were held constant. This was accomplished with p- and m-substituted phenyl bearing dioxetanes. The steric question was probed to a small extent with some cis/trans-isomeric dioxetanes.

Originally we anticipated a correlation of triplet efficiencies (as log α_T) with conventional LFER substituent parameters such as σ or σ^+. For example, in the simplified thermolysis mechanism shown below, k_{s_o} should increase with electron releasing aryl substituents while k_{isc} should not be

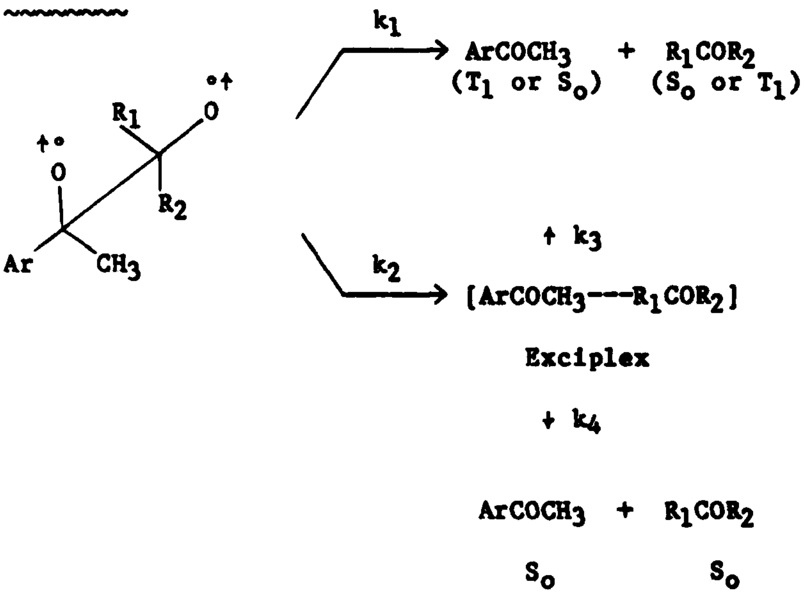
Scheme 1



particularly sensitive to substituent effects. From this, one is lead to expect a LFER with log % α_T vs σ or σ^+ where ρ is positive. In contrast to this expectation, correlations with σ or σ^+ failed. Instead, the best correlation was observed with log $\%\alpha_T$ vs $E_{T_1}(ArCOCH_3)$, where the latter term is the lowest triplet energy of the acetophenone product.

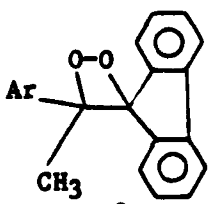
In the correlations with log$\%\alpha_T$ vs $E_{T_1}(ArCOCH_3)$, the slope (S) was positive, so that decreasing $E_{T_1}(ArCOCH_3)$ corresponds to lower α_T values. This is the reverse of what might be expected, ie, decreasing $E_{T_1}(ArCOCH_3)$ would seem to facilitate triplet carbonyl formation. To rationalize this observation, an exciplex mechanism was proposed. This is shown below as it proceeds from the triplet biradical. According to this mechanism, triplet

Scheme 2



energy wastage occurs via the exciplex, where this species can give excited state (k_3) or ground state (k_4, energy wastage) products. It is proposed that by lowering $E_{T_1}(ArCOCH_3)$, the energy of the exciplex decreases to favor k_2 relative to k_1. Thus, lowering $E_{T_1}(ArCOCH_3)$ results in lower α_T values.

To test the exciplex proposal, additional dioxetane series 2, 3, and 4



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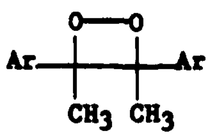

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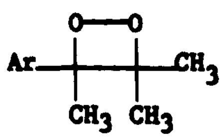

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were studied. The exciplex mechanism suggests that both pro-carbonyl moeities in the dioxetane should effect the stability of the exciplex and thus α_T. The above set of substituted dioxetanes was selected where a pro-acetophenone moeity is present in each case. The companion pro-ketone has triplet energies that are higher (cf, 4), equal (cf, 3) and lower (cf, 2) than $ArCOCH_3$.

In an attempt to measure triplet efficiencies of 2 by the 9,10-dibromoanthracene (DBA) method, no enhanced light emission was noted by the addition of DBA. This method was previously used to measure α_T for dioxetane 1 without difficulty. Independent photoexcitation studies also showed that efficient energy transfer to DBA from $ArCOCH_3$ occurred. We could then conclude that 2 did not produce triplet $ArCOCH_3$ products. However, α_T could be measured via isomerization of the low energy triplet (<50 kcal/mol) acceptor t-stilbene. These observations are reasonable only if fluorenone (E_{T_1} = 53 kcal/mol) is produced from 2, since these triplets are too low in energy to transfer energy to DBA ($E_{S_1} \cong 70$ kcal/mol) by the triplet, singlet process.

Yet, triplet, triplet energy transfer to t-stilbene from fluorenone is favorably exothermic.

The α_T values for 2 were effected significantly by substituent changes in the pro-acetophenone portion of the molecule. The $\%\alpha_T$ values ranged from 2% (2, Ar=p-BrC_6H_4) to 19% (2, Ar=C_6H_5) and represent the specific fluorenone triplet efficiency. As was observed with 1, the best correlation of these data was with log $\%\alpha_T$ vs $E_{T_1}(ArCOCH_3)$. The exciplex mechanism readily explains the

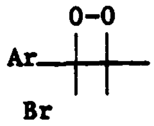
communication of substituent effects in the pro-acetophenone moeity of 2 to the pro-fluorenone moeity.

Triplet efficiencies were readily measured by the DBA method for 3. Again, the best correlation was with log$\%\alpha_T$ vs $E_{T_1}(ArCOCH_3)$ for cis-3. An

unusual result was obtained here, namely, the α_T values for cis- and trans-3 (Ar = C_6H_5) differed (cis = 44%, trans = 52%). This is most readily explained in terms of the exciplex mechanism (Scheme 2) whereby k_1/k_2 differs for the two isomers. From this, it follows that the stability of the exciplex derived from the two isomers differs. Assuming a head-to-tail array of the carbonyl group in the exciplex, molecular models do show different steric effects. It was mentioned previously that steric effects alter triplet efficiencies and possibly the exciplex may be the key to explaining this observation. We plan to pursue this idea in the future.

Activation parameters and substituent effects for thermolysis of dioxetanes 1, 2, and 3 support a stepwise biradical mechanism. With a σ^+ correlation, the ρ-values are 1 (−0.321 ± .056), 3 (−0.285 ± .033), and 2 (0.0800 ± .0454). The near-zero ρ-values are consistent with only O-O bond rupture in the activated complex. Large negative ρ-values are expected for a concerted decomposition.

Synthesis of series 4 dioxetanes proved difficult when the aryl group contained electron releasing substituents. Instead of isolating 2 by the conventional synthetic route (olefin to bromohydroperoxide (BHP) to dioxetane), the bromodioxetane 5 was obtained when Ar contained electron releasing groups.



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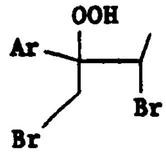

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It was deduced that the BHP sample contained a small amount of the dibromo hydroperoxide 6, which gave 5 upon treatment with a silver salt.

For both 5 (electron releasing aryl groups) and 4 (electron withdrawing aryl groups), there is little variation in α_T. The average $\%\alpha_T$ value is about 28%. That is, the S-value is approximately zero for the $\log\%\alpha_T$ vs $E_{T_1}(ArCOCH_3)$ correlation.

We can now consider the trend in S-values for series 1 (0.378 ± .139), 2 (0.518 ± .079), 3 (0.696 ± .216), and 4/5 (~0) dioxetanes. Although the data set is limited and the error is large, it appears that the largest S-value occurs when the two pro-ketone moeities are equal as in 3. When the two carbonyl moeities are the same, the triplet exciplex as defined by the two canonical structures in 7, will have particular stability. It is under this

$$[{}^*ArCOCH_3 \cdot R_1COR_2 \longleftrightarrow ArCOCH_3 \cdot {}^*R_1COR_2]$$

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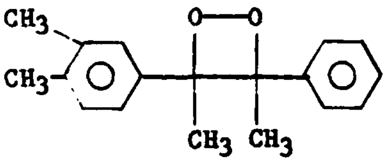
circumstance that the aryl substituents exert a maximum effect on α_T. The next largest S-value is associated with 2, where the very low triplet energy of fluorenone (53 kcal/mol) may be responsible for the stability of the exciplex. For 1, the $ArCOCH_3$ triplet energies are somewhat higher and lower than CH_2O(E_{T_1} = 72.5 kcal/mol). Although the S-value for 1 is lower than that of 2 or 3, it is significant. The similarity in triplet energies of the two carbonyl products may impart some particular stability to the exciplex as in 1.

However, when acetone was the companion ketone product to the acetophenone (as in 4) or phenacyl bromide (as in 5), the S-value is approximately zero. Considering Scheme 2, this may represent an increase in the k_1/k_2 ratio compared to the other dioxetane series 1, 2, and 3. As the stability of the exciplex decreases, path k_1 is expected to be favored relative to k_2. This is what is expected when acetone (E_{T_1} = 80 kcal/mol) is the companion carbonyl product. With a higher triplet energy, acetone destabilizes the exciplex. Furthermore, decreasing $E_{T_1}(ArCOCH_3)$ is expected to <u>increase</u> α_T for path k_1, where this path is also in competition with the k_{-isc}, k_s, path (Scheme 1). This is in contrast to the k_2 path where decreasing $E_{T_1}(ArCOCH_3)$ <u>decreases</u> α_T. Thus, the k_1 and k_2 paths show opposite responses to α_T with changing E_{T_1} ($ArCOCH_3$) values. Presumeably such a balance is struck with 4 or 5, such that $S \cong 0$.

Another interesting difference with series 5 dioxetanes is that high singlet efficiencies (α_{S_1}) are observed. For series 3 dioxetanes, the highest α_{S_1} value is about 2%, while for 5 the α_{S_1} values are about 9%. Possibly a heavy atom effect is operative here, either at the biradical or the exciplex step in the mechanism.

State Selectivity Effect. Work from other laboratories (eg, Zimmerman, et al, J. Am. Chem. Soc., 1976, 98, 5574.) has raised the question of state-selectivity in the production of triplet carbonyl products from dioxetanes. That is, are n,π^* states selectively produced rather than the lowest triplet state when this state is π,π^*? To test this proposal, we have determined the total triplet efficiency of 8 by the DBA method. Here state selectively (n,π^*) predicts preferentially formation of 10, while non-state selectivity (lowest triplet) predicts 9. Depending on whether the state selectivity on non-state selectivity route is followed, a different total triplet efficiency is expected for 8.



----> $3,4\text{-}(CH_3)_2C_6H_3C(=O)CH_3$ + $C_6H_5C(=O)CH_3$

9 10

8 (cis or trans)

		9	10
E_T(kcal/mol)	n,π^*	74.2	73.4
	$\pi\,\pi^*$	72.2	75.5

One can estimate the total triplet efficiency of 8 in the following manner. The energy distribution between the ketone products 9 and 10 can be estimated by the Boltzmann equation 1 (cf, Richardson, Lovett, Price, and Anderegg, J. Am. Chem. Soc., 1979, 101, 4683.). For n,π^* state selectivity

$$E_T(9) - E_T(10) = RT\ln \alpha_T(10)/\alpha_T(9) \qquad (1)$$

$E_T(9)$ and $E_T(10)$ are 74.2 and 73.4 kcal/mol, respectively; while for non-state selectivity (ie, lowest triplet state) $E_T(9)$ and $E_T(10)$ are 74.2 and 73.4 kcal/mol, respectively. With equation 1, the distribution for state selectivity is 76% 10 and 24% 9; while for non-state selectivity the distribution is 15% 10 and 85% 9. Now equations 2 and 3 can be formulated to calculate the total triplet efficiency of 8 by state selectivity (α_T(SS)) and by non-state selectivity (α_T(non-SS)).

$$\alpha_T(\text{SS}) = 0.76\,\alpha_T\,(3\ \text{Ar} = C_6H_5) + 0.24\,\alpha_T\,(3\ \text{Ar} = 3,4\text{-Me}_2C_6H_3) \qquad (2)$$

$$\alpha_T(\text{non-SS}) = 0.15\,\alpha_T\,(3\ \text{Ar} = C_6H_5) + 0.85\,\alpha_T\,(3\ \text{Ar} = 3,4\text{-Me}_2C_6H_3) \qquad (3)$$

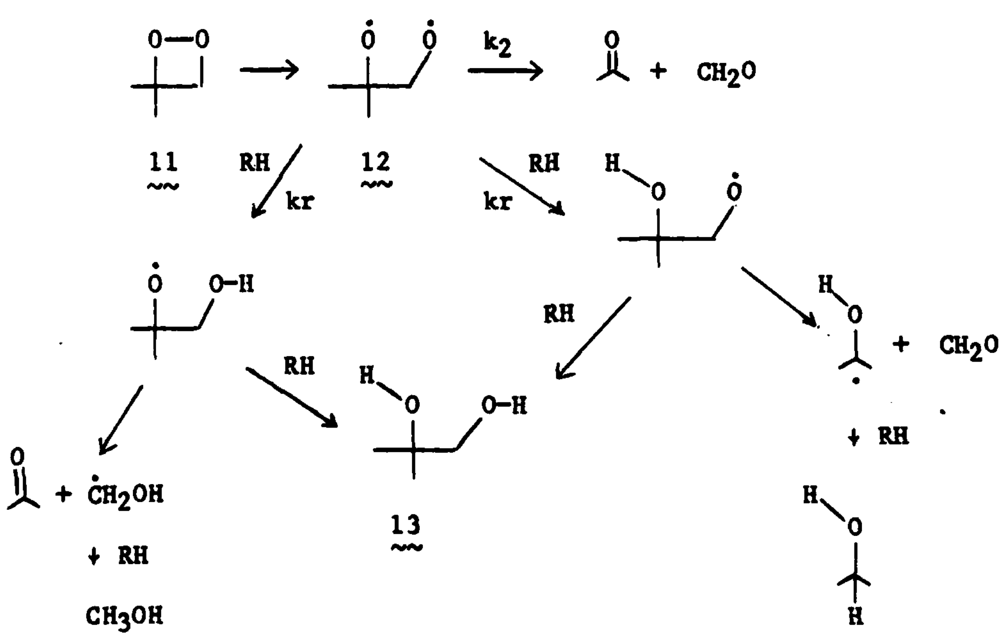
The efficiencies for the series cis-3 dioxetanes in equations 2 and 3 were previously measured, so that α_T(SS) and α_T(non-SS) can be calculated. The calculated values are α_T(SS) = 35% and α_T(non-SS) = 12%. These values can be compared to the measured value for cis-8 of α_T(obs) = 14%. Thus, the agreement between calculated and observed α_T-values is quite good for non-state selectivity (lowest triplet, here π,π^*) and deviates significantly from the state selectivity estimate. The α_T(trans-3 Ar = C_6H_5) value is available (52%), but a value for α_T (trans-3 Ar = $Me_2C_6H_3$) is not available. An estimate of this latter efficiency can be made based on α_T (trans-3 Ar = C_6H_5)/α_T(cis-3 Ar = C_6H_5)(=52.0/43.9) and α_T (cis-3 Ar = $Me_2C_6H_3$)(=6.24), ie, α_T (trans-3 Ar = $Me_2C_6H_3$) = (52.0/43.9) x 6.24 = 7.4%. The efficiencies α_T(SS) and α_T(non-SS) are calculated as outlined above. The values of α(SS) and α(non-SS) are 41% and 14%, while the observed value for trans-8 is 21%. Again, the best agreement is with non-state selectivity.

The difference in efficiency between cis and trans isomers is noted here again with 8. The observed efficiencies with error are: α_T(Obsd, cis-8) = 14.1 ± .2% and α_T (Obsd, trans-8) = 21.3 ± .5%. The two efficiencies are then not within our experimental error. As stated above, we feel that this difference in α_T may be due to steric effects in the exciplex.

Biradical Trapping. Although the substituent effect data, that was discussed above, suggests a 1,4-dioxybiradical decomposition path for simply substituted dioxetanes, there is as yet no direct evidence for this intermediate. In addition, other workers have proposed a concerted decomposition path with little C-C bond breaking in the activated complex. Thus, direct evidence for the 1,4 dioxybiradical intermediate is desirable.

Trapping experiments were carried out with 1,4-cyclohexadiene and this is exemplified with 3,3-dimethyl-1,2-dioxetane (11) in Scheme 3. Triplet carbonyl

Scheme 3



quenchers (eg, t-stilbene) were used to avoid hydrogen atom abstraction by the triplet carbonyls. The lifetime of biradical 12 ($\tau = 1/k_2$) can be calculated from equation 5, which is derived from equation 4. Here, the (% Yield Trapped

$$(\%\ \text{Yield Acetone})/(\%\text{Yield Trapped Products}) = \frac{k_2[12]}{k_r[RH][12]} \qquad (4)$$

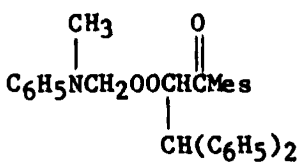
$$k_2 = \frac{k_r\ (\%\ \text{Yield Acetone})[RH]}{(\%\ \text{Yield Trapped Products})} \qquad (5)$$

Products) is the sum of the yields of glycol 13, i-propyl alcohol, and methanol. The yields of these products and acetone were determined by GC. The k_r value is obtained from the literature and taken as twice the rate of alkoxy radical H-atom abstraction from 1,4-cyclohexadiene.

The above treatment yielded τ for biradical 12 in the nano-second region, which was in the range of an earlier prediction (Richardson, Montgomery, Yelvington, and O'Neal, J. Am. Chem. Soc., 1974, 96, 7525.). Similar studies have been carried out with trimethyl-, tetramethyl-, and 3,3-dibenzyl-1,2-dioxetane.

A possible difficulty with these results is the observation of an enhanced rate of dioxetane decomposition in the presence of 1,4-cyclohexadiene. The enhanced rate could be due to induced decomposition of the dioxetane. If so, the origin of some of the "trapped products" could be questioned. Some preliminary data suggests that the major portion of the "trapped products" are not the result of induced decompositions. Further experiments are required to confirm this conclusion, whereby plots of % yield vs initial dioxetane concentration are made for all of the products. Extrapolation to zero dioxetane concentration in this plot will represent % yields of products that are free of induced decomposition.

Potential CL Amino Peroxides. We have examined a few peroxides that contain the amino group and which possess sufficient energy to generate excited state carbonyl products. The amino peroxides 14 (Mes = mesityl), 15, and 16 were prepared. Weak CL was observed during the thermolysis of these peroxides



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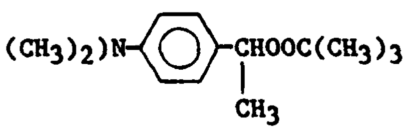

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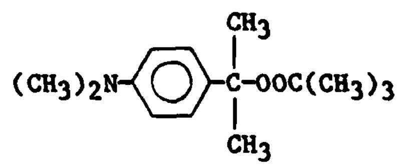

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in the presence of acceptors (DBA, 9,10-diphenylanthracene, and rubrene). However, it was concluded that the CL resulted from autoxidation and not from the carbonyl products of these peroxides. This demonstrated that in addition to sufficient energy to generate excited state species, a correct reaction path is also required. The details of these studies are given in published reports (Richardson, J. Org. Chem., 1980, 45, 303; Richardson and Thomson, ibid., 1982, 47, 4515.).

The Mechanism of Thermolysis of a Five-Ring Peroxide. A report from another laboratory suggested that five-membered ring peroxides (1,2-dioxolanes) undergo a concerted thermal decomposition. If this is correct, then four-membered ring peroxides (1,2-dioxetanes) would be even more prone to a concerted decomposition. Since our work suggested a stepwise biradical thermolysis path for 1,2-dioxetanes, we were motivated to reinvestigate the thermolysis of 3,3,5,5-tetramethyl-1,2-dixolane. It was found that this peroxide was very sensitive to induced decomposition. This is reasonable upon examining molecular models which show an exposed peroxide group. When induced decomposition was largely circumvented, activation parameters resulted that were consistent with a stepwise biradical decomposition route. The details of this work can be consulted in a published report (Richardson, McGuinness, O'Neal, J. Org. Chem., **1981**, 46, 1887.).

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